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(54) **Sol-gel composition containing hydrolysable silicic ester for producing glassy coatings**

(57) Glassy coatings are made by curing in situ a coating of a sol gel, xerogel or heat-consolidated gel composition comprising a hydrolysable silicic ester, 1-4 moles water per mole of silicon and a solvent e.g. alcohol, filled with a filler such as kaolinite or with flat plates (1-2 μ m x 10-50 μ m) of mica, which may be coated with TiO₂, Cr₂O₃ or Fe₂O₃ applied by CVD. The silicic ester may be silicon tetrahalide or tetraalkoxysilicon. Further fillers are laponite, zeolite, talc, vermiculite. The mica or talc may be coated with silane. The composition may also contain a metal alkoxide capable of participating in forming glass structures with the silicic ester, e.g. alkoxides of Na, Zr, Al and Ti. The composition may be cured to form the glassy coating by the use of laser radiation or a butane gas flame. Use is made of very miniature flames so as to avoid vital tissue when curing on a tooth. Part of the silicic ester may be replaced with other glass formers such as boron-based sol gels.

The coating may be applied to teeth as a dental fissure sealant or varnish to protect restorations, or as an inherently coloured cosmetic coating, or as a prophylactic coating. In an application for slow drug release the coating may be charged with a drug, eg for treating dentine hypersensitivity or periodontal disease.

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SOL GEL COMPOSITION FOR
PRODUCING GLASSY COATINGS

This invention relates to a sol gel composition for use in producing glassy coatings, to a process for producing a glassy coating using the composition, to a method for cosmetic colouring of teeth using the process and to a method for prophylactic protection of teeth using the process.

Fissure sealants have been demonstrated as effective in reducing incidence of tooth decay and inhibiting decay even after
05 it has started, but have not gained universal acceptance in general practice. These fissure sealants are understood to have relatively low durability, adhering to the tooth with a rather short half-life (5 years).

Sol-gels would not be considered for dental use, since the
10 curing of sol gels is typically undertaken in a slow furnace, which would pose clinical difficulties. Japanese Patent Publication 1083671 (published 29 March 1989), in the name of Kobe Steel, proposes a calcium phosphate sol gel, but for coating artificial teeth to be subsequently embedded in the human body.

15 According to the invention, a sol gel, xerogel or heat-consolidated gel composition comprises a hydrolysable silicic ester (such as silicon tetrahalide or tetraalkoxysilicon), 1 (preferably 1½) - 4 moles water (which may be added later) per mole of silicon, a solvent (alcoholic or
20 non-alcoholic) and a filler, such as laponite, zeolite, kaolinite or vermiculite, or preferably a filler in the form of flat plates such as talc or mica, or a mixture, optionally coated (preferably by chemical vapour deposition) with for example titanium dioxide, chromium oxide or ferric oxide or a mixture, the filler
25 preferably amounting to up to 30% by weight based on the gel. Part of the silicic ester can be substituted by appropriate compounds of other non-metallic glass formers. Other coating methods may also be used, alternatively or in addition, such as deposition of silane. This can promote adhesion and enhance

mechanical properties. As silanising agents, compounds containing a glycidoxy group and a polyalkoxy (e.g. trimethoxy) silyl group may be used, for example Dow Corning Z6040 (trade mark), $(\text{CH}_3\text{-O-})_3\text{Si-(CH}_2)_3\text{OCH}_2\text{-CH-CH}_2$.

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- 05 Also according to the invention, a coated composition comprises a hydrolysed and cured silicic ester containing a filler as set forth above. Such filler materials are harmless if swallowed in the small quantities in which they might spill off. The mean filler particle size is preferably up to $3\mu\text{m}$ (e.g. 0.1 to $2\mu\text{m}$) in
10 one dimension and $5\text{-}100\mu\text{m}$ in the other two dimensions. Where the latter dimensions are $5\text{-}20\mu\text{m}$, the filler preferably comprises from 20 to 30% by weight of the composition, and where those dimensions are $10\text{-}60\mu\text{m}$, the filler preferably comprises 10-20% by weight of the composition. Cross-laid fibres may be used. In
15 the case of xerogel, which is 90 volume % air, a platey filler will improve its mechanical properties such that it could be used as an insulating material, or the cavities can be used as drug reservoirs, which will slowly release, on a tooth or otherwise.

- The filler reduces the incidence of crazing in the cured
20 sol-gel (not only in dental applications) by physically reducing the bulk of sol gel needed, thus making what there is of it more elastic. It also absorbs incident laser energy and re-emits it to the sol gel, accelerating the latter's curing. The filler also improves the abrasion resistance of the cured sol gel glassy
25 coating. Given that the yield of glass from sol-gels is preferably about 5-10% by weight, and can be 0.1 to 1% or even less the filler will thus be a major component of the product. In the case of mica, which tends to fall out of sol-gel suspension quite rapidly, it may be incorporated into the sol-gel
30 when or immediately after the latter is made up; as the sol-gel 'polymerises', the polymers grow on the mica, improving its suspension and bonding, but as a precaution it may be advisable to shake it before use, or else the mica may be added to the sol gel at any later stage, e.g. immediately before use. On the

other hand, a too-perfect suspension is to be avoided; as it is, the mica advantageously settles into pits and fissures, whither it is drawn by surface tension.

The hydrolysable silicic ester is preferably
05 tetraethoxysilicon. The molar proportion of water:silicon is preferably (1½ to 3):1, for example 1½:1 or 2:1. Part of the Si, as already mentioned can be substituted by appropriate compounds of other non-metallic glass formers along the lines of the teachings of for example Brinker and Scherer "Sol Gel Science"
10 ISBN 0-12-134970-5, Academic Press 1990, pp 78-95 and Sowman at pp 162-165 in "Sol-Gel Technology for thin films (etc)" ISBN 0-8155-1154-X, Noyes Publications USA, 1988, about boron-based sol gels, as precursors for which such compounds as boron alkoxide, boric acid, boron nitrates or boron citrate, optionally
15 esterified, are suggested. The solvent may comprise hydrophobic materials such as partly or wholly halogenated methane, e.g. CCl₄, or tetrahydrofuran, or diethylether, or hydrophilic materials such as ketones e.g. acetone or alcohols e.g. ethanol optionally containing up to an equal volume of propanol
20 (iso or n) preferably from ½ to ¾ volumes (e.g. 60 ethanol:40propanol). The proportion of water plus solvent may be such that the composition yields 1-10g silica per 100 g (the filler being included in the 100 g). In an alternative sol-gel preparation method, solvents (including
25 water) may be absent and an intermediate solid may be converted into an applyable liquid sol gel composition by controlled exposure to atmospheric moisture.

Preferably one or more metal alkoxides are present capable of participating in forming glassy structures with the silicic
30 ester, such as sodium, zirconium, aluminium or titanium alkoxide singly or in any combination, such as Si+Al+Ti+Na or Si+Zr+Na, with all these metals (not counting Na) being present in preferred amounts of up to 20%. Solid oxides e.g. fine neodymium oxide powder may be dispersed into the sol gel. In the sol gel
35 synthesis, there is preferably an ageing step, during which moisture is admitted to the composition at a rate under 1% of the rate in free air. This controls the rate of hydrolysis and consequently of 'polymerisation' of the molecules of the composition without destabilisation, which rate can in principle

be monitored via an increase in viscosity of the composition, or e.g. by differential scanning calorimetry, by thermogravimetric analysis, by nuclear magnetic resonance or by electron spin resonance.

- 05 A process for producing a glassy coating according to the invention comprises applying a sol gel composition e.g. as set forth above, to an object to be coated and curing the coating e.g. by radiation from the tip of a diathermy needle or by flame e.g. butane flame heating, (very miniature flames can be used in
- 10 the mouth), otherwise preferably by laser, for example a CO₂ laser, with an energy input to the object of preferably 200 to 1000 J/cm² preferably applied at a rate which does not cause overheating leading to cracking or flaking of the film, such as under 4W (more preferably up to 1W) per mm², e.g. 0.2 to
- 15 0.8W/mm, preferably for a duration of 1 to 4 (e.g. 2 to 3) seconds i.e. in the region of ¼-3 J/mm². A CO₂ laser may be tuned to 10.6µm as is most usual, or may be tuned to or near 9.6µm (e.g. 9¼-10µm), which is most strongly absorbed by natural tooth. This is useful if it is desired to fuse
- 20 (physically incorporate) the sol gel into the enamel, which also fuses, a procedure which requires high laser power outputs and an appropriate filler, and which is expected to make the enamel more resistant to caries. The pulse width and frequency can be varied to suit the thickness of the film to achieve good consolidation.
- 25 This energy input is found to raise the tooth temperature by only 1-2C°, excess heat being removed by the blood supply to the pulp. An Nd:YAG (1.06µm) laser could be used, but needs a chromophore in the sol gel to absorb it. The coating (after curing) may be up to 30µm thick, preferably 2-10µm.
- 30 A method for cosmetic colouring of a tooth according to the invention comprises using the process set forth above, wherein the said object is the tooth. The tooth may have been treated with restorative material such as glass alkenoate cement, for

which the present invention can be regarded as providing a varnish. The sol-gel may include a pigment. The neodymium oxide powder suggested above imparts a remarkably evenly distributed blue colour to the glass. Alternatively, the filler may be so formulated as to appear a tooth-like colour in the applied thickness. Alternatively, the tooth is stained cosmetically, and the stain retained by the applied coating. As a side-effect, prophylactic benefits may be obtained.

A method for prophylactic protection of a tooth according to the invention comprises using the process set forth above, wherein the said object is the tooth. The tooth may have been treated with restorative material such as glass alkenoate cement, for which the present invention can be regarded as providing a protection. Preferably the filler is so formulated as to appear a tooth-like colour in the applied thickness. As a side-effect in that case, cosmetic benefits may be obtained. In all these methods, where the filler permits, the option (explained above) of fusing the enamel, at least superficially, may be adopted.

Preferably the tooth is cleaned beforehand e.g. mechanically or by acid-etching.

The present invention provides a method whereby drugs may be released slowly, comprising allowing a coating produced by xerogel as set forth above and charged with the drug to ablate.

The two forms of product derived from sol-gel, viz glass and xerogel, differ in the physical organisation of their polymeric structures:

(i) Sol-Gel derived glass: A high density polycondensed SiO_2 lattice or network with minimal porosity.

(ii) Sol-Gel derived xerogel: A polymeric structure which is highly porous in the 100nm range and of correspondingly low density, having trapped organic residues and being mechanically weak. The formation of a xerogel is a direct indication of sufficient hydrolysis to yield a useful glass material. The deposition of a thin film from these sol-gels will depend upon dilution factor and nature of the solvents used. It is important to note these sol-gels once synthesised will continue to undergo hydrolysis and condensation.

Defect free glassy films are important for adequate tooth protection, and require careful attention to two crucial stages in the sol-gel process once a continuous liquid coating has been applied:

- 05 (i) Sol liquid-to-gel transition
- (ii) Consolidation of gel to glass.

Stage (i) needs to be slow which implies controlled rate of solvent loss, otherwise the shrinkage of resulting gel is rapid and uneven leading to a fractured coating. The gel has to be
10 partially dried and then given even surface heat treatment. Stage (ii), viz heat treatment, also needs to be carefully controlled, otherwise the film will crack and/or blister. The glass coating is vulnerable to cracking during heat treatment where shrinkage occurs, as density increases, mainly in the
15 vertical direction and not the horizontal. Thin coatings that are less than $\frac{1}{2}\mu\text{m}$ generally do not suffer from cracking and have better mechanical durability. Following this finding, efforts to develop a sol gel glass having the same coefficient of thermal expansion as natural tooth were discontinued as unnecessary.

20 Using liquid spreading techniques likely to be available in ordinary clinical practice would however yield coatings on tooth surfaces having a thickness of approximately 5-10 μm . (Applying a drop from a dropwise dispenser, it spreads across the tooth surface spontaneously.) As indicated above, the addition of a
25 filler is necessary e.g. an inert filler such as mica flakes; it permits thicker yet crack-free consolidated glass coatings and improves xerogel coatings.

Sol-gel derived coatings may be applied to:-

- (i) Fissure sealing
- 30 (ii) Sealing marginal gaps arising from old restorations
- (iii) Entire tooth crown surface protection
- (iv) Root canal therapy, e.g. sealing tubules
- (v) Lining freshly prepared cavities (blocking open
 tubules)

- (vi) Protection of cavities freshly restored with filling materials
- (vii) Replacing the use of porcelain veneers for aesthetically coating discoloured enamel surfaces
- 05 (viii) Slow release of fluoride for topical application to tooth
- (ix) Controlled release of drugs for example in the treatment of dentine hypersensitivity or periodontal disease, and
- 10 (x) Impregnation of porous structures, subject to the filler, for mechanical strengthening and other purposes e.g. drug release, enamel disorders and dental material improvement.

There are certain preferred ranges of compositions of the sol-gel. Considering atoms of Si, Na (or equivalent), Al, Zr and Ti (or equivalent), silicon preferably accounts for at least 30, more preferably at least 40%. Sodium is preferably under 50% (on an atomic basis again) such as 1 - 40%, more preferably 5 - 30%. Aluminium may be 5 - 15%, and Gp VB and IVB, such as titanium and/or zirconium and/or vanadium and/or niobium and/or tantalum 3 - 15%, more preferably 5 - 10%, and/or not exceeding one-sixth of the silicon. Silicon is desirable as a glass-former, and sodium should be limited as it makes the glass less resistant to acid.

25 The invention will now be described by way of example.

A multicomponent sol gel was prepared containing:

(Example 1): $\text{Si}(\text{OEt})_4$, NaOMe and $\text{Zr}(\text{O-n Pr})_4$ (Comparative)

(Example 2): $\text{Si}(\text{OEt})_4$, NaOMe and $\text{Al}(\text{O-secBu})_3$ (Comparative)

The synthesis conditions greatly affect the final properties, and in these Examples the preparation involved carrying out all reactions and mixing in a moisture free atmosphere (glove box and/or a vacuum line apparatus with dry N_2 atmosphere). Any

medically acceptable solvents could be used. All the alkoxides were made up separately in ethanol. Tetraethoxysilicate (TEOS, $\text{Si}(\text{OCH}_2\text{CH}_3)_4$) was partly hydrolysed by adding a limited amount of water, ($\text{H}_2\text{O} : \text{Si}(\text{OCH}_2\text{CH}_3)_4 = 2:1$ moles) and maintained at 70°C for 2 hours (normally equimolar water is added). If the theoretical amount of 4 moles water per mole of TEOS (pH 6) is used, cosolvents such as ethanol with isopropanol will be found necessary. With gentle refluxing for a short time, such as 2 hours or less, a sol-gel should result stable at room temperature for at least 2 months and even longer at 0°C . Some of the $\text{Si-O-CH}_2\text{CH}_3$ groups became hydrolysed to Si-OH and ethanol.

First the sodium ethoxide (4.7g) (dissolved in anhydrous ethanol) was added to TEOS (21.9g) followed by 4.3g Zr-propoxide (Example 1) both being in 17.5g ethanol (anhydrous). A yellow/orange coloured liquid was formed. Example 2 was similar, with Al replacing Zr mole for mole.

After 24 hours the sol showed no sign of turbidity or any precipitation or gelling at room temperature. The sol-gel made in this way appeared to be stable for 6-12 weeks. Addition of a few drops of water (approximately 1ml) to the sol-gel (approximately 3-4ml) resulted in rapid gelling, with the formation of a light orange gel. The gel was left to dry out at room temperature leaving a pale yellow-orange xerogel.

The conversion of gel to xerogel at room temperature results only in partial hydrolysis of TEOS. Only a proportion of the expected SiO_2 was incorporated into the glass. The chemical composition of the xerogel was found by X-ray diffraction analysis to be SiO_2 64%, Na_2O 24% and ZrO_2 12%.

Both yielded two types of coating, a xerogel incomplete conversion of metal alkoxide to oxide resulting in a low density highly porous (nm range pore size) material, and glass the coating consists of metal oxide in the form of a glassy lattice with negligible levels of metal alkoxide/residues.

The transformation or polymerization of the liquid sol gel to a gel state requires the loss of solvents and finally polycondensation to the consolidated glass state. This can be achieved by a hot air dryer or by infra-red laser absorbed by silica glass i.e. laser wavelength $> 2\mu\text{m}$, such as CO_2 or Er:YAG or Ho:YAG (yttrium aluminium garnet) laser. The CO_2 laser may be tunable (rather than fixed at $10.6\mu\text{m}$) if it is desired to make use of the fact, which comes into its own when using a transparent filler, that absorption by natural enamel of radiation of $\lambda = 9.6\mu\text{m}$ is many tens of times that at $\lambda = 10.6\mu\text{m}$. For lower-wavelength lasers, a chromophore should be used to absorb the laser energy. To absorb the radiation of the latter, the sol gel included 0.1-5 weight % of a transition ion salt being any one or more of cupric nitrate, cupric sulphate, chromium (III) chloride, chromium (V) oxide and potassium permanaganate, and an energy input of $100\text{J}/\text{mm}^2$ was required, too much for intra-oral use.

Using cw CO_2 laser ($10.6\mu\text{m}$), conversion of gel to glass was complete, producing a coating which appeared to be totally resistant to 0.5M (usually only 0.02M is used for tests) of lactic acid even after 16 weeks. Normally only 0.02M concentration is used in conventional studies. CO_2 lasers have the property that their output is strongly absorbed by glass, virtually all the energy being absorbed within a thickness of 30 microns.

The sol gels of Examples 1 and 2 have been modified by loading inert fillers to make Examples 3 and 4 respectively, according to the invention. Inert fillers such as ceramic colours of particle size $2-10\mu\text{m}$ (1-5 weight %) were used but tended to settle out of the sol gel with time. Small particles of mica were successfully loaded and greatly improved the quality of the coating and its mechanical properties.

The mica had the form of plates 1-2 μ m thick and 10-50 μ m in the other two dimensions, with 95% by volume of the particles being under 38.1 μ m, half under 21.1 μ m and 5% under 11.6 μ m, with a heavy preponderance around 15-25 μ m. The mica was fully coated
05 with a layer of Fe₂O₃, then a layer of TiO₂, or the other way round, or either one, which controlled the colour and is believed to have assisted bonding with the sol-gel (which itself bonds to natural tooth chemically rather than purely physically). It was
10 found that the mica plates lay in place well, parallel to and adapting to the tooth surface.

EXAMPLE 5

A silica sol-gel was formulated to yield 10% SiO₂ using tetraethoxysilicate (TEOS). The solvents used were ethanol, propan-1-ol, deionised water and as catalyst 0.01-0.04M hydrochloric acid.

A molar ratio of 1 TEOS: 4 H₂O was gently refluxed for 125 minutes at pH \approx 6 to hydrolyse it. The boiling point of the sol-gel was dependent on the ratio of individual components, the range being 72 to 84°C. The silica sol-gel made in this was was
 05 stable at room temperature for a week or so. With less water (the above amount being adequate for complete hydrolysis), the sol-gel could be stable more or less indefinitely.

The quantities of the constituents were:

		Calculated	Used
10	TEOS	41.6g	44.5ml
	Water	14.4g	15.13g
	Ethanol	28.7g	28.7g
	Propan-1-ol	19.6g	19.6g
	3M HCl	25 μ l	30 μ l [\equiv 0.02M in the total volume, which was 120ml].

15 The above sol-gel was modified by adding mica as a filler. The various micas used are listed by particle size (diameter of flat surface) and chemical nature of their coating:

	Particle size	Coating Type	Appearance	% used by weight total	Coating Quality
20	10-60 μ m	TiO ₂ (Anatase)	Silver pearl	15	Good
	10-60 μ m	TiO ₂ (Rutile)	Silvery	15	Good
	2-20 μ m	TiO ₂ (Anatase)	Lustre satin	30	Good
	40-200 μ m	TiO ₂ (Anatase)	Flash pearl	10	Poor
	40-200 μ m	TiO ₂ (Anatase)	Shimmer pearl	10	Poor
25	10-60 μ m	TiO ₂ (Rutile)	Lilac pearl	15	Good
	10-60 μ m	Fe ₂ O ₃	Royal Gold	15	Good
	10-60 μ m	Fe ₂ O ₃	Bronze	15	Good
	10-60 μ m	Fe ₂ O ₃	Red	15	Good

Mica is a naturally occurring aluminosilicate ($\text{KA}_2(\text{AlSi}_3\text{O}_{10})\text{OH}$). Its surface even in the uncoated state is thought to become chemically bonded to the glassy matrix. The hydroxy groups take part in Mica-O-Si bond formation. Only a
05 very thin covering of gel is present over and in between the mica plates, and this reduces the tendency of the glass resulting from the gel to suffer from stress-relief cracking.

The physical properties of mica, that is good thermal and electrical insulation, high mechanical resistance, and low
10 coefficient of friction, may also contribute to the lack of sol-gel cracking. Furthermore, the mica plates or flakes are oriented parallel to the surface on which the thickness of the coating has been applied, and this will arrest crack propagation normal to the surface, since such a crack must suffer lengthy
15 'detours' around the mica plates i.e. fracture length has been greatly increased.

The sol-gels were applied to air-dried mechanically cleaned (equivalent to sand blasted) tooth surface via an analogous method to dip-coating. One to three drops (approximately
20 100-300 μl) of the sol-gel were deposited on to the tooth surface, a single drop sufficing for the whole occlusal surface. The liquid was spread over the surface with a jet of compressed air or a chip syringe. This simple method generated a thin coat of liquid. Compressed air thinning serves three important functions:
25 (i) Sol-Gel was forced into small crevices, pits and fissures

(ii) Excess sol is removed leaving a very thin film of liquid on the surface

(iii) Solvents are evaporated off and atmospheric moisture
30 catalyses hydrolysis and condensation resulting in polymeric gel formation.

The liquid readily flowed and wetted all surfaces evaluated (acid etched/EDTA cleaned or unprepared enamel, dentine, amalgam, glass ionomer and composite restoratives).

05 The remaining solvents and water in the gel, after compressed air thinning, required to be carefully removed. The gel was dried with a hair dryer at an air temperature of 50-60°C or 60-70°C for 5-10s. The specimens were moved back and forth in the hot air stream at an approximate rate of 3-5cm/s (for a short distance into and out of the air stream).

10 Typically, the applied dry-weight gel loading over the surface was 7-13 μ g/mm², equivalent to a consolidated coating thickness of the order of 10¹ microns.

Drying the gel further induces hydrolysis and condensation and the silica-oxygen system progresses to a glassy state.

15 The coating became semitranslucent, tacky and "gel-like". This gel state was the result of hydrolysis and condensation; with large "-O-Si-O-" polymer unit formation. If the gel was allowed to dry out at room temperature or at 37°C for at least 5-10 minutes it formed a xerogel having a porous structure with
20 incomplete hydrolysis and condensation of Si-OH and Si-O-CH₂CH₃ groups. The xerogel coating appeared to be continuous, with some degree of fracture, and was transparent/lustrous. In section the xerogel coating thickness was in the region of 1 to 30 μ m. When scratching the surface with a dental probe, drag indentation
25 marks were left.

Thicker coatings were produced by multiple deposition of gel and xerogel. Xerogels derived from multiple gel or gel-xerogel-gel layers could not be distinguished as individual layers with SEM analysis. The multiple coated surface appeared
30 as a single coating. Up to 3-4 coats could be applied, and above this number severe surface crazing resulted.

The polymeric gel state requires heat treatment to produce the collapsed molecular structure free of pores and organic residues, that is a glass. Clinical applications require the heat treatment process to avoid vital tissue. Three methods of

05 heat treatment were tried:-

(i) cw IR laser radiation at $1.06\mu\text{m}$ (cw = continuous wave)

(ii) cw IR laser radiation at $10.6\mu\text{m}$

(iii) Butane gas flame

(i) $1.06\mu\text{m}$ Laser

10 Continuous wave Nd:YAG laser radiation, powers up to 20W, did not consolidate the sol-gels. This was due to very low absorption of the $1.06\mu\text{m}$ radiation. In order to enhance absorption the sol-gel was modified by the addition of dissolvable transition ion salts as in Examples 1 and 2.

15 As a consequence of high temperature rises the high energy input resulted in the tooth becoming hot to handle and the tooth enamel tended to fracture.

(ii) $10.6\mu\text{m}$ Laser

20 Warm air dried ($60-70^\circ\text{C}$) sol-gels were consolidated on the tooth surface at low irradiance ($40-100\text{W}/\text{cm}^2$) at exposure durations of 100ms to 1s. Multiple laser exposures (2-3 at 1Hz) were necessary to consolidate the gel fully, the surface appearing lustrous and transparent to the naked eye. Scanning electron micrography revealed the surface to be smooth and
25 featureless but with an appreciable degree of fracture. A crimped surface pattern was common in pits and fissures.

When a consolidated surface was scratched with a dental probe the surface fractured like glass. Clean, well defined edges were produced. The consolidated surface appeared smooth and
30 featureless and no pores were detected at a $1\mu\text{m}$ resolution. The following cw CO_2 laser parameters were found to produce good

consolidated glass with minimal film cracking and without any damage to the tooth detectable by scanning electron microscopy:

$$\begin{array}{l} \text{cw Laser Power: 5 to 6W} \\ \text{Exposure duration: 0.8s} \\ \text{Pulsing rate: 1Hz} \\ \text{Number of exposures: 2-3} \\ \text{Spot size: 3-4mm diameter} \approx 7 \text{ to } 12 \text{ mm}^2 \end{array} \left. \vphantom{\begin{array}{l} \text{cw Laser Power: 5 to 6W} \\ \text{Exposure duration: 0.8s} \\ \text{Pulsing rate: 1Hz} \\ \text{Number of exposures: 2-3} \\ \text{Spot size: 3-4mm diameter} \approx 7 \text{ to } 12 \text{ mm}^2 \end{array}} \right\} = 4.0 \text{ to } 4.8 \text{ W} \left. \vphantom{\begin{array}{l} \text{cw Laser Power: 5 to 6W} \\ \text{Exposure duration: 0.8s} \\ \text{Pulsing rate: 1Hz} \\ \text{Number of exposures: 2-3} \\ \text{Spot size: 3-4mm diameter} \approx 7 \text{ to } 12 \text{ mm}^2 \end{array}} \right\} \text{ about } \frac{1}{2} - \frac{3}{4} \text{ W/mm}^2$$

Excessive laser heat treatment by means of higher irradiance (greater than approximately 150 W/cm^2) and or multiple laser exposures (4-6 pulses, 1-2Hz, at 100ms to 5sec) produced excessive crazing and cracking and blistering of the coating.

One successfully used laser was a continuous wave CO_2 laser emitting a maximum of 20W at $10.6 \mu\text{m}$, whose beam was focussed such that the spot size was $(0.2 \text{ mm})^2$ and whose beam was scanned on the substrate in zig-zag mode, such that the spot traversed its own diameter in 0.1 milliseconds while advancing steadily at such a rate that after one complete zigzag (1 cycle) it had returned to an area exactly abutting its original location. In this way, every point on the tooth surface received two and only two periods of illumination, each lasting 0.1 ms. It was found preferable to illuminate each point twice rather than once (even when the total energy input per unit area was the same), and scanning modes allowing four or six separate periods of illumination have also been successful. The following procedure was carried out experimentally on extracted ^{human} teeth for sol-gel consolidation followed by vitrification and was found to be advantageous in generating a good subsurface vitreous structure without adverse thermal and mechanical defects to the tooth as a whole:

The tooth was dip coated and allowed to drip dry on adsorbent paper and or warm air dried.

The surface of the tooth was then scanned using the above laser scanning parameters, but at a low power (below 5W). This is to gently warm the sol-gel thin film and evaporate solvents and water. The surface may be scanned several times; 2-5 scans
05 is normally sufficient (dependent upon the solvent/water content of the gel).

The power is increased to 8-12W to fully consolidate the gel to a glassy film. Several (two to four) scans may be necessary. If the <5W procedure is not followed then the gel is
10 vaporized/ablated from the tooth surface whereby subsequent vitrification of the enamel surface will contain only small amounts of silica. In this way, a firm glassy film containing filler is applied to the tooth, which itself remains unmodified.

The power input to the sol gel is preferably 25 to 500, e.g.
15 40 to 250 W/cm², and may be higher as long as the substrate be not damaged; the energy input per period of illumination is preferably at least 1J/cm², more preferably at least 10J/cm².

An alternative laser, avoiding the problems of scanning, has a large spot (as large as the tooth, whose environs would be
20 masked); this is the transversely excited atmospheric CO₂ laser.

Multiple thin films could be built up by consolidation of individual gel layers. The resultant coating also tended to be fractured through the full thickness of the coating. The individual layers of glass were only distinguishable when the
25 surface was scratched. However, the glass-glass boundary appeared to be continuous with the absence of gaps.

(iii) Butane

The temperature of butane (CH₃CH₂CH₂CH₃) gas burning with a blue flame (approaching complete combustion to CO₂ and H₂O) is near
30 1000°C. Exposing a material surface of negligible heat capacity, such as sol-gel glass coatings of 10µm thickness, may cause surface temperature rises in the region of 800 to 1000°C. Such

temperatures may be used to consolidate the "gel" state to a glass. The associated events would be initial evaporation and combustion of organic residues, accompanied by simultaneous collapse of the SiO_2 structure to a glass monolith.

05 Sol-gel coated specimens were, momentarily, exposed to the blue part of a butane bunsen flame. The specimens were moved horizontally through the flame at a rate of 6-8 cm/s for 2-4s. The specimens became warm but not hot to the touch.

10 Sol-gel coatings on enamel, dentine, restorative materials, silicon wafer substrates and glass slides could all be consolidated to a glassy film without excessive heating. The consolidated glassy film was smooth and featureless with little cracking. However, at longer flame exposure durations (approximately 3-6s) or slower rate of traverse through the flame
15 (less than 6cm/s), severe film cracking resulted with flaking and blistering of the glassy coating. Specimens of teeth become warm, but not hot to the touch, during the brisk flame consolidation.

20 In appearance the converted film was similar if not identical to that produced by consolidation with the CO_2 -laser heat-treated sol-gel.

These cured sol-gel coatings were then subjected to 'accelerated attack', namely exposure to 0.5M lactic acid at 37C for 30 days.

25 Flame-consolidated films on glass slides and on silicon wafers lost 20% of their weight and the physical appearance changed becoming opaque (with possible precipitation of SiO_2 and or break down of polymeric structure). However, improved results were obtained using 5 seconds' exposure to 1100°C. CO_2 -laser
30 consolidated films as set forth above remained transparent at all times and did not dissolve. Continuous wave CO_2 laser irradiation for 100-500ms on a spot size of 2mm diameter

(corresponding irradiance $200\text{W}/\text{cm}^2$) was also found to consolidate silica sol-gel films. The laser beam in the chopped mode (20Hz, 25-45ms pulse duration) could also consolidate sol-gel coatings to a lactic-acid-resistant glass. Xerogels cured for 10 hours or
05 more did not lose weight and remained transparent. This applied also to exposure for 16 weeks to 0.5M lactic acid, or exposure to fuming nitric acid, or to 30% orthophosphoric acid (= dental etchant). The films were resistant to scratching by anything other than a diamond burr.

10 In de-ionised water, the bulk of flame-consolidated sol-gel films remained unchanged. However, their surface layer became opaque and white; xerogels remained transparent.

Organic solvents such as ethanol, propanol, ethanone, or methoxymethane were found not to dissolve either the flame
15 consolidated coatings or the xerogel. The coated surface remained smooth and featureless.

An accelerated wear test using a toothbrush weighted to 360g rubbing the CO_2 -laser-consolidated sol-gel coating under water at 190 strokes per minute removed about 95% of the coating after
20 24 hours. From this, assuming that normal brushing occurs for 20 seconds daily on each surface, a coating life of about 12 years may be expected, as a very approximate guide.

EXAMPLE 6

A silica sol-gel was formulated to yield initially 10% SiO_2
25 using the same silicon source, solvents and catalyst as Example 5.

The following mixture (totalling 100ml) was made up and refluxed for 2½ hours:

	Calculated	Used
TEOS	32g (1 mole)	34.45g
30 H_2O	5.53g (2 mole)	5.60g
Propan-1-ol	25g	25.32g
Ethanol	37.48g	37.68g
3M HCl	20μl	20μl
(i.e. 0.0006M final solution)		

These quantities of alcohol should not be exceeded until after the refluxing, which gave rise to a sol-gel stable at room temperature and capable of yielding 10% SiO_2 . After the refluxing, it was then possible to incorporate mica and to dilute the sol-gel further, e.g. tenfold or even a hundredfold, in for example ethanol, propanol or other solvent suitable for the surface being coated. The loaded and diluted sol-gel, stored in sealed glass vessels, has remained usable to create a mica-filled thin film after eighteen months' storage at both -10°C and room temperature.

EXAMPLE 7

The following components were mixed:

Na ethoxide 21.5g

TEOS 104.05g

15 Al sec-butoxide 17.4g

Ti tetra-isopropoxide 20.42g

After a year's storage at -10°C , this was found to have separated into a clear viscous liquid above a semisolid phase. Such samples would normally be rejected, but we have discovered that this is unnecessary. The liquid can successfully be used in its own right loaded with filler, or else the sample can be allowed limited access to moisture at room temperature (e.g. by providing apertures in the seal), when it will be found that after a day or so the liquid becomes less viscous and eventually dissolves all the semisolid phase, yielding a stable sol-gel liquid. The separation can be entirely avoided by exposing the freshly prepared mixture to room humidity for 2-3 weeks and then sealing it; such a sample has remained a stable liquid for over a year.

30 EXAMPLE 8

The object was to make a solventless sol-gel, of intended composition (by weight): SiO_2 60.3%; Na_2O 16.83%; Al_2O_3 13.3%; ZrO_2 9.4%

The following components were assembled:

	Calculated	Used
TEOS	98g	99.62g
Zr tetra-sec-butoxide	13.875g	13.79g
05 Al tri-sec-butoxide	16.01g	19.87g
Na ethoxide	9.2g	9.3g

The following procedure was carried out in a dry nitrogen atmosphere. The TEOS and Zr salt (a yellow viscous liquid) were mixed and readily yielded a stable clear yellow liquid. The Al salt was added, resulting in a white precipitate/suspension, which may consist of Al triethoxide (which can form from the components present). The Na ethoxide, a yellow powder, is added and mixed for one hour, and, after settling, results in a clear liquid above a semi-transparent viscous orange layer, the lower part of which is gelatinous, above a layer of white granules. This is not a clear usable sol-gel!

However, after exposure of this to limited atmospheric moisture for 19 days, the mixture unexpectedly becomes totally clear, even the granules being resorbed, yielding a slightly viscous orange-tinted sol-gel, which, if left fully open to the atmosphere, eventually turns into a glassy xerogel. Mica could be added immediately after the sodium ethoxide.

EXAMPLE 9

Somewhat akin to the foregoing example, a $\text{SiO}_2+\text{Zr}+\text{Al}+\text{Na}+\text{Ti}$ sol-gel was made up using the following ingredients: TEOS 12.27g (actual); Zr tetra-sec-butoxide 1.70g; Al tri-sec-butoxide 2.45g; Na ethoxide 1.14g; and Ti isopropoxide 6.1g. To a mixture of the TEOS and the Zr salt, the Al salt was added with mixing, then the Na salt. After 1 hour's agitation, a viscous yellow-orange suspension resulted, to which the Ti salt

was added with no ill effects; the mixture remained a suspension but also some material settled out as in the previous example. After 2-3 weeks' exposure to limited atmospheric moisture, a clear sol-gel liquid resulted, which is considered likely to remain stable for at least a year when stored either at -10°C or at room temperature, under sealed conditions. This liquid produces a glassy xerogel.

In an experiment, the Al tri-sec-butoxide was replaced by Al-tri-propoxide, which gave inferior results, possibly because it (the propoxide) was faster reacting, leading to faster hydrolysis and hence more undesirable precipitation.

CLAIMS

1. A sol gel, xerogel or heat-consolidated gel composition, comprising a hydrolysable silicic ester, 1-4 moles water per mole of silicon, a solvent and a filler.
2. A composition according to Claim 1, wherein the silicic ester
05 is silicon tetrahalide or tetraalkoxysilicon.
3. A composition according to Claim 1 or 2, wherein the filler is laponite, zeolite, kaolinite or vermiculite.
4. A composition according to Claim 1 or 2, wherein the filler is in the form of flat plates.
- 10 5. A composition according to Claim 4, wherein the plates are talc or mica.
6. A composition according to Claim 4 or 5, wherein the plates are coated.
7. A composition according to Claim 6, wherein the plates are
15 coated with titanium dioxide, chromium oxide or ferric oxide or a mixture.
8. A composition according to Claim 6 or 7, wherein the plates are coated by chemical vapour deposition.
9. A composition according to Claim 6 or 7, wherein the plates
20 are coated with silane.
10. A composition according to any of Claims 4 to 9, wherein the filler additionally comprises laponite, zeolite, kaolinite or vermiculite.
11. A composition according to any preceding claim, wherein the
25 filler amounts to up to 30% by weight based on the gel.
12. A coated composition comprising a hydrolysed and cured silicic ester containing a filler as respectively defined in any preceding claim.
13. A composition according to any preceding claim, wherein the
30 filler particle size is up to $3\mu\text{m}$ in one dimension and from 5 to $100\mu\text{m}$ in the other two dimensions.
14. A composition according to Claim 13, wherein the filler comprises from 20 to 30% by weight of the composition and the platey particles are 5- $20\mu\text{m}$ across.

15. A composition according to Claim 14, wherein the filler comprises from 10 to 20% by weight of the composition and the platey particles are 10-60 μ m across.
- 05 16. A composition according to any preceding claim, wherein the solvent comprises a ketone or one or more alcohols.
17. A composition according to any preceding claim, further comprising one or more metal alkoxides capable of participating in forming glassy structures with the silicic ester.
- 10 18. A composition according to Claim 17, wherein the metal alkoxides are any one, two or more of: a Gp IA metal, a Gp IVB metal, and Gp VB metal and Al.
19. A composition according to Claim 18, wherein the metal alkoxides present are any one or more of Na, Zr, Al and Ti.
- 15 20. A composition according to Claim 19, wherein the metal alkoxides present are: Al+Ti+Na; or Zr+Na.
21. A composition according to Claim 18, wherein, counting atoms of Si and metal, at least 30% of the atoms are silicon, under 50% of the atoms are sodium, 0 or 5-15% are aluminium, and not exceeding one-sixth of the silicon and/or 3-15% are Gp IVB and/or
- 20 Gp VB.
22. A composition according to any preceding claim, comprising 1% to 3 moles water per mole of silicon.
23. A composition according to any preceding claim, further comprising a non-metallic glass former (other than Si).
- 25 24. A process for producing a glassy coating comprising applying a composition according to any preceding claim, to an object to be coated and curing the coating.
25. A process according to Claim 24, wherein the coating is cured by laser.
- 30 26. A process according to Claim 25, wherein the energy input to the object is 200 to 1000 J/cm².
27. A process according to Claim 25 or 26, wherein the power input to the object is under 4W/mm².

28. A process according to any of Claims 24 to 27, wherein the coating is up to 30 μ m thick.
29. A method for cosmetic colouring of a tooth, comprising performing a process according to any of Claims 24 to 28, wherein
05 said object is the tooth, and wherein the tooth is either stained cosmetically beforehand and the stain retained by the coating, or the composition contains a colour.
30. A method for prophylactic protection of a tooth, comprising performing a process according to any of Claims 24 to 28, wherein
10 said object is the tooth.
31. A method of slow drug release, comprising applying a coating charged with the drug to a tooth by a process according to any of Claims 24 to 28, and allowing the coating to ablate.
32. A process according to any of Claims 24 to 28, wherein the
15 said object is a patient's tooth.

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Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

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Relevant Technical fields

- (i) UK Cl (Edition K) C7F (FHD, FHZ); C3T
- (ii) Int Cl (Edition 5) C23C; C01B

Search Examiner

P G BEDDOE

Databases (see over)

- (i) UK Patent Office
- (ii) ONLINE DATABASES: WPI

Date of Search

27 AUGUST 1992

Documents considered relevant following a search in respect of claims 1-32

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1257656 A (CORNING) see especially Example 1	1,24
X,P	EP 0490433 A1 (AKZO) see especially Claim 1; Example 1	1,24
X	EP 0064344 A1 (MOBIL) see especially page 5 lines 16-27; page 10 lines 5-34	1,24
X	JP 630017976 A (NIPPON) see Derwent English Language abstract (WPI Acc No : 88/066499/10)	1,24
X	JP 610235469 A (NIKKI) see Derwent English Language abstract (WPI Acc No : 86/316282/48)	1,24
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SF2(p)

TP - doc99\fil000293

Category	Identity of document and relevant passages	Relevant to claim? (✓/✗)

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Patents Act 1977
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(i) UK CI (Edition) Contd. from page 1

(ii) Int CI (Edition)

Databases (see over)

(i) UK Patent Office

(ii)

Search Examiner

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Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	US 4378996 A (CLINO) see especially Claim 1 and Examples at page 2	1, 24

SF2(p)

TP - doc99\fil000293

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